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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Appl. No.   : 10/659,577   Confirmation No. 4666

Applicant   : Lawrence T. Drzal and Hiroyuki Fukushima

Title   : EXPANDED GRAPHITE AND PRODUCTS PRODUCED
                 THEREFROM

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Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 C.F.R. § 1.132

Dear Sir:

        Lawrence T. Drzal states as follows:

(1.)   That he is an inventor of the invention in the

above entitled application.

-1-

(2.)   That he is the Director of the Composite Materials & Structures Center and a Professor of Chemical Engineering and Materials Science and Mechanics at Michigan State University, East Lansing, Michigan 48824.
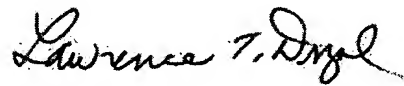
(3.)   That unlike the teachings of U.S. Patent No. 6,024,900 to Saito *et al.*, the precursor graphite in the above entitled application is expanded within a microwave or radiofrequency wave applicator.

(4.)   That chapter 2 of the dissertation of Hiroyuki Fukushima, entitled "Exfoliated Process for Graphite Intercalation Compounds", attached as Exhibit A, illustrates that graphite expanded by a microwave process has superior properties as compared to graphite expanded by a heat treatment.

(5.)   That graphite expanded by a microwave process has a higher degree of expansion and has a cleaner surface than graphite expanded by a heat treatment.

(6.)   That the undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Lawrence T. Drzal

_____
Lawrence T. Drzal

Date: 06-21-06
_____

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EXHIBIT A

CHAPTER 2.

EXFOLIATION PROCESS

FOR

GRAPHITE INTERCALATION COMPOUNDS

2.1. Introduction

Graphite is one of the strongest and stiffest materials found in nature. Recent discovery of new nano-size graphite materials, such as fullerene and carbon nanotubes, are attracting attention because of their superior mechanical, electrical, thermal and other properties. [1, 2] These materials are expected to be used in many applications such as advanced composites for high strength structural materials, high conductive materials for EMI shielding and fuel cell parts, anode materials for batteries, and hydrogen fuel storage. One main drawback of these nano-size graphite materials is their high cost. The cost of nanotubes is in the $50-500/g ($22,700-227,000/lb) range, depending on the structure and purity of the material. It is obvious that this material is still too expensive for many commercial applications.

Crystalline graphite has excellent mechanical, electrical, and thermal properties. Many crystalline graphite materials are available including natural and synthetic forms. These materials are more abundant and more economical than graphite whiskers and VGCF. Pure crystalline graphite has similar or better properties than these materials [3]. Carbon nanotubes have better properties than these crystalline graphite materials, yet the costs of nanotubes are far beyond the level for commercial applications. [4] If nanosize crystalline graphite flakes can be produced at a reasonable cost, the material can be used in many commercial applications because of its excellent mechanical, thermal, and electrical properties.

Graphite has been known as a host material for many chemicals, including metal halides, metal oxides, and mineral acids. The exfoliation phenomena of the graphite intercalated compounds (GIC) have been investigated for a long time. Aylsworth filed

two patents related to expanded graphite and its usage in molding application in the 1910's. [5, 6] The claims include (1) the process of intercalating acids into graphite, (2) heat expansion of the intercalated graphite to make "fluffy graphite", and (3) compounding expanded graphite in resins, typically phenolic resins. Since then, many researches have been investigating the exfoliation of GICs [7, 8, 9, 10, 11]. Chung wrote a review about the exfoliation phenomena of GICs [12].

There are several methods to expand GICs. The most commonly used technique is the rapid heating in a furnace. This is widely used in the commercial stage. Other methods can include infrared, laser, microwave, and electric current. Among these, microwave systems are available in many sizes and power levels, yet very little has been investigated about microwave exfoliation of GICs. In this research, natural crystalline graphite-based acid intercalated graphite compounds were exfoliated by heating or a microwave processes. The effects of temperature, microwave power, and the size of graphite flakes on degree of expansion were examined by XRD. Also the surface chemistry of the exfoliated graphite samples was investigated by XPS. It revealed that the microwave process could give a better degree of expansion and a cleaner surface at lower cost. These expanded graphite samples were pulverized and milled into sub-micron graphite flakes. SEM and TEM images showed that the average size of graphite became 0.86um and the thickness of around 10 nm. The cost of this new nano-size graphite material was estimated to be around $5/lb. With its superior mechanical, electrical, thermal properties and cost effectiveness, this material could be used in variety of applications such as nanocomposites, secondary batteries, and fuel cells.

2.2. Experiment

2.2.1. Graphite Materials

The graphite samples used in this research were Graphite Intercalate Compounds (GICs), which were acid intercalated natural crystalline graphite flakes offered from UCAR Inc. The acid components consist of sulfuric and nitric acid. Nitric acid acts as an oxidizer while sulfuric acid acts as an intercalant. The acid intercalated graphite exhibits multiple stages, ranging from stage 1 to 5. The stage number indicates the number of graphene sheets between adjacent intercalated galleries. Upon heating, the intercalated acids become vapor and force layers apart, causing exfoliation of graphite layers. The sample grades used in this research are Grafguard™ 160-50A, 160-50B, and 160-50N. Here "160" refers to the onset temperature at which intercalated acid begins to be released and exfoliation of the graphite occurs. "50" indicates the average size of the flakes is 50 mesh, which is 300 um. A, B, and N show the conditions of the sample surface, which are acidic, basic, and neutral.

2.2.2. Measurements

- Thermogravimetric Analysis (TGA)

A Cahn TG System 121 analyzer was used for thermogravimetric analysis. 10 to 20mg of GICs were heated up to 800°C at the rate of 10°C/min. The weight loss was monitored and the acid intercalate content was determined.

- X-Ray Diffraction (XRD)

A Rigaku rotaflex 200B diffractometer was used for XRD analysis. The X-ray source was Cu-Kα with a curved graphite monochromator. The operational setting was

45kV and 100mA. The diffraction patterns were collected from 1° to 60° (2θ) at a scanning rate of 3°/min.

Since graphite materials have a layered structure, they show characteristic peaks in their XRD patterns. Among these, the peak from d002 is the highest and most distinctive one, appearing at 2θ = 26.5° or 0.335 nm. The height of the d002 peak is a measure of how many layers are stacking together to form graphite flakes. Thus, the degree of exfoliation was investigated by measuring the d002 peak height after the exfoliation process.

■   X-Ray Photoelectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA)

X-ray photoelectron spectra were obtained from a Physical Electronics PHI 5400 ESCA system. A non-monochromatic Mg source (with a $K_{\alpha1,2}$ wavelength at 1253.6 eV) was used with a take-off angle of 45 degrees. Data was collected by a multi-channel detector with an Omni VI lens assembly. The instrument was operated with a pass energy of 93.90 eV for survey scans and 29.35 eV for regional scans. All peaks were referenced to adventitious carbon at 284.6 eV. Semi quantitative atomic concentrations were calculated using pre-determined sensitivity factors. XPS samples were prepared by applying the graphite directly to double sided copper tape on a stainless steel stub.

XPS analysis was used to investigate the acid remaining on the surface of exfoliated graphite. The sulfur and nitrogen content of graphite suggest the existence of sulfuric and nitric acid, since pure natural crystalline graphite has no or very little amount of these atoms on its surface.

- Environmental Scanning Electron Microscopy (ESEM)

ElectroScan 2020 environmental SEM (ESEM™) outfitted with a LaB_6 filament was used for SEM analysis. GSED detector with a 1.0 mm bore was used. Working condition of electron-beam energy was 20 kV, a working distance was 10 mm, and a chamber pressure was 3 Torr. SEM images of expanded and exfoliated graphite were taken to investigate the physical structure, morphology, and size of the graphite flakes. The diameter of a few hundred flakes was measured and a size distribution curve was established.

- Transmission Electron Microscope (TEM)

Hitachi H-8100 TEM or JEOL 2010F with 200 kV electron-beam energy microscope was used to investigate the nanoscale structure of the exfoliated graphite samples.

- BET Surface Area Measurement

Micromeritics TRISTAR 3000 was used to analyze the surface areas of reinforcement materials. Each sample was outgassed at 250°C under 0.1 torr for 12 hours prior to the measurement, except the as-received graphite sample. Since this sample has acid intercalates which can evaporate at 160°C, it was dried at 150°C. BET surface areas were determined from the region between P/P_0 of 0 to 0.2. Eight data points were collected for each sample and an average value was calculated. Error margins for the measurements were determined by using standard samples with similar surface areas.

2.3. Results and Discussion

2.3.1. Expansion of Graphite Flakes by Heating

Figure 2.1 is a TGA data that shows the expansion condition of 160-50A. It revealed that initial expansion occurs around 160°C, but most of it occurs in the range of 250 to 350 °C. The amount of acid intercalated in 160-50A was determined at around 21 wt%. 160-50N showed almost the same tendency in TGA curves but has less acid intercalates, around 16wt%. 160-50B showed a slightly different degradation curve, showing two steps in the weight loss curve. This sample has base on its surface that could affect this result. The acid content of 160-50B is around 12wt%. During the expansion process, a graphite flake expands 100 to 1000 times in c-axis direction and makes a worm-like shape with flakes attached together [**Figure 2.2**]. This sample was defined as expanded graphite. Since 160-50A has the largest amount of acid and shows the highest degree of expansion, this research mainly used 160-50A as the starting material.

Two factors affect the degree of expansion: temperature and the size of the graphite flakes. To investigate the effect of temperature, 4g of 160-50A was exfoliated at 300, 400, 500, 600, 700, 800, 900, and 1000°C for 3 min. **Figure 2.3** shows the image of the expanded graphite samples after the treatment. This image reveals that the degree of expansion increased as temperature increased up to 600°C, then it reached a plateau beyond that temperature. Thus, it is concluded that the temperature of 600°C or higher is required to achieve maximum degree of expansion. This also agrees with literature citations indicate that temperatures above 800°C were used to expand acid intercalated graphite flakes in their research [13, 14, 15, 16, 17].

To investigate the effect of size, 160-50A flakes were sieved into different sizes, less than 25um, 25 to 75um, 75 to 106um, 106 to 180um, 180 to 300um, 300 to 500 um, and over 500 um. 0.1 g of each sample was dispersed in a crucible and expanded at 900 °C for 5 min at the same time in the same furnace. **Figure 2.4** shows the image of expanded graphite after the heat treatment. The larger the sample size is, the larger the degree of expansion is. This is because the vaporized intercalate escapes from the edge region, rather than pushes the layers apart, when the size of the flake is small. Also TGA data revealed that the smaller graphite has less acid intercalates, which should lead less expansion (**Figure 2.5**). Judging from these experiments, it is concluded that graphite flakes of 75 um or larger size show good expansion, and those of 180 um or larger show the maximum expansion.
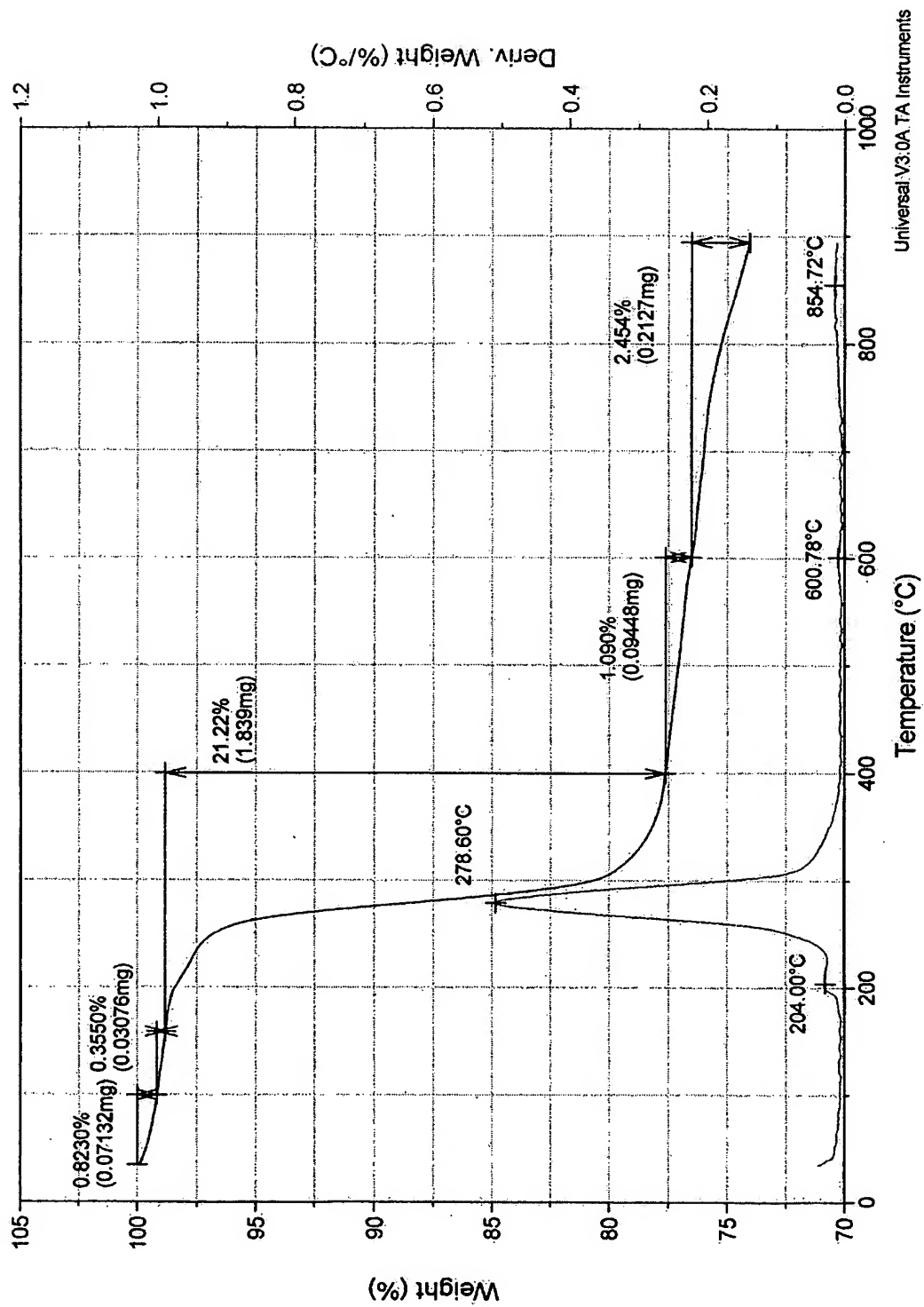
Figure 2.1. TGA Data of Acid Intercalated Graphite Sample (160-50A)
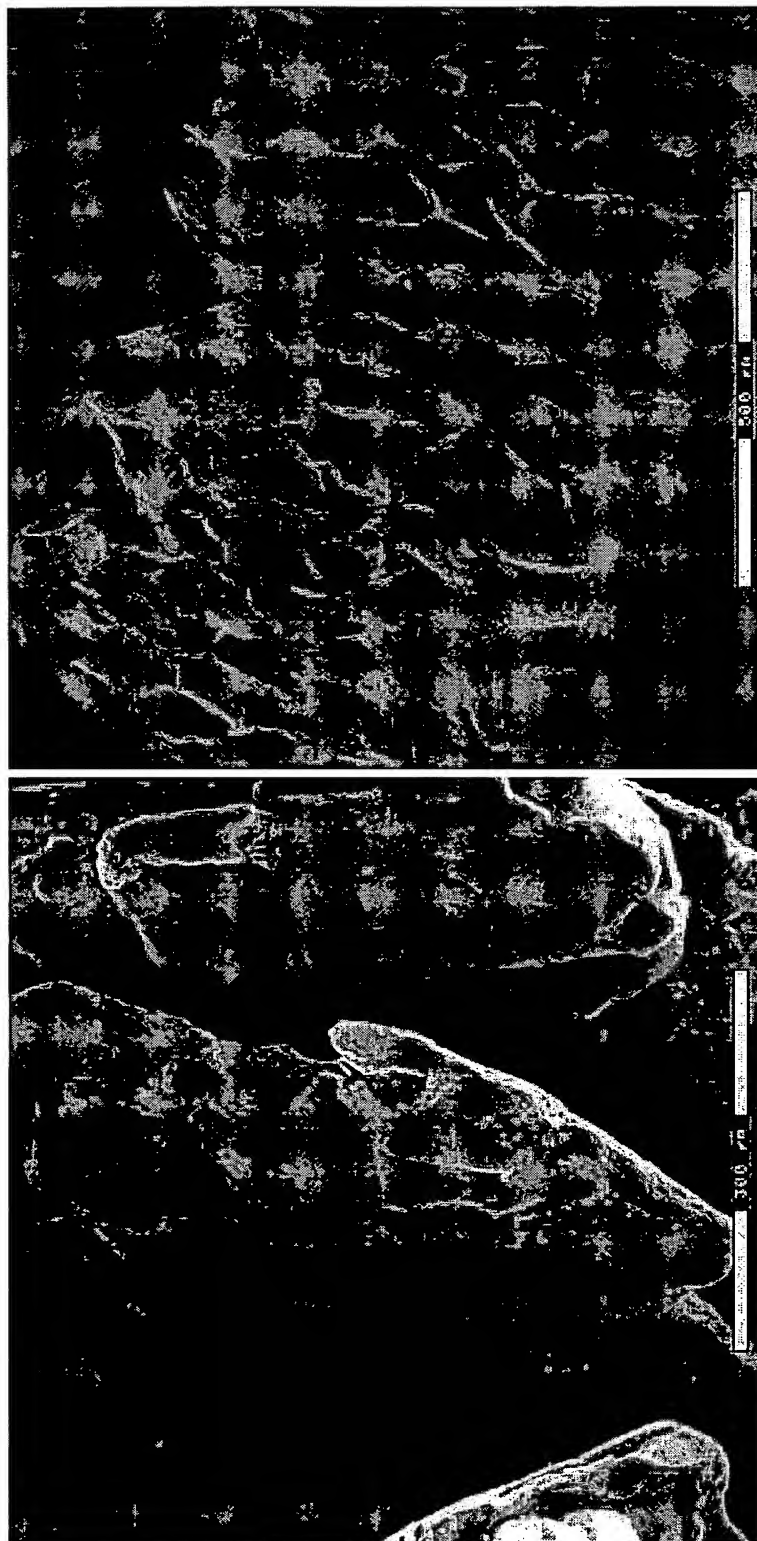
Figure 2.2. ESEM images of as-received 160-50A (left) and expanded graphite at 900°C (right). (Scale Bar = 500 um)
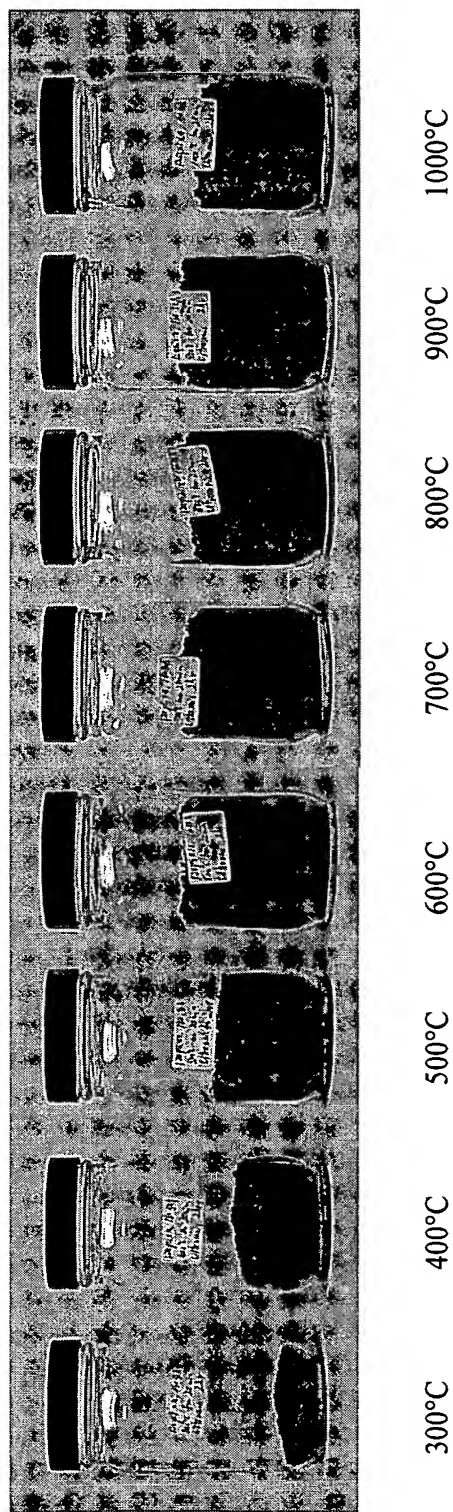
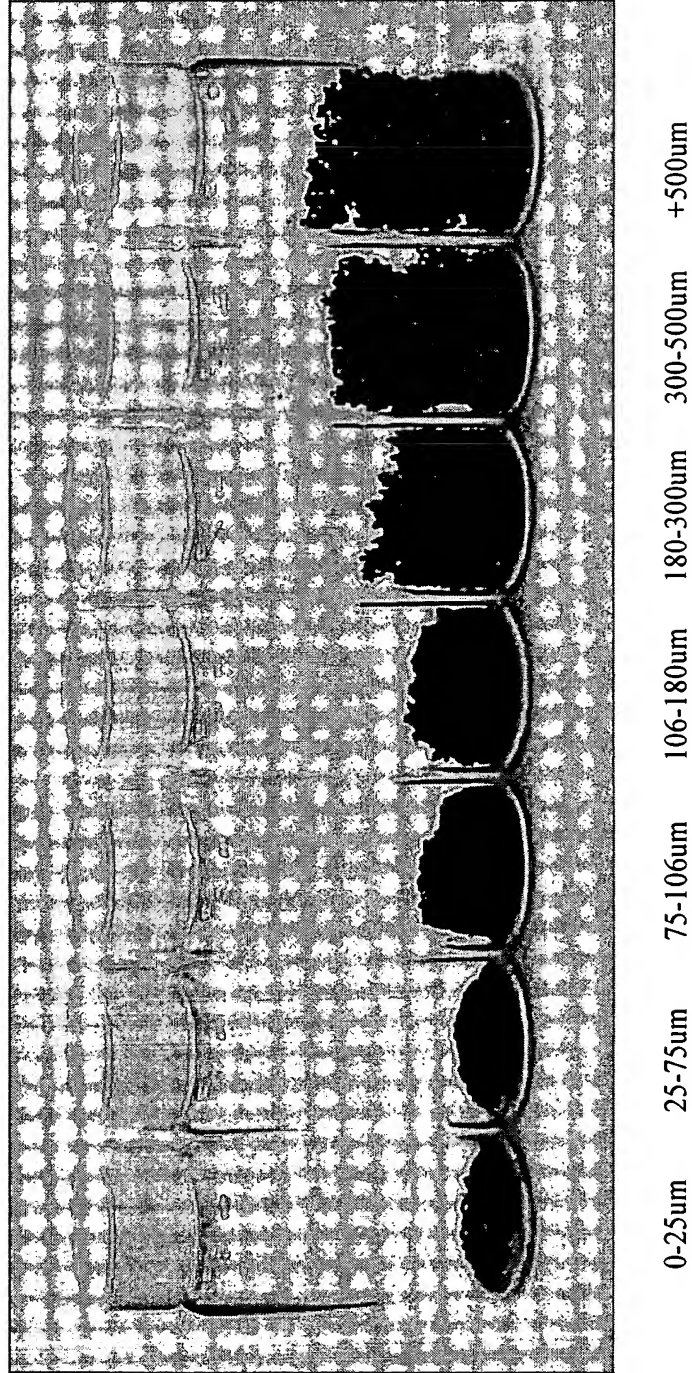Figure 2.3. The Effect of Temperature on Degree of Expansion (160-50A)

300°C   400°C   500°C   600°C   700°C   800°C   900°C   1000°C

Figure 2.4. The Effect of Size on Degree of Expansion (Heating Process at 900°C.)

0-25um   25-75um   75-106um   106-180um   180-300um   300-500um   +500um
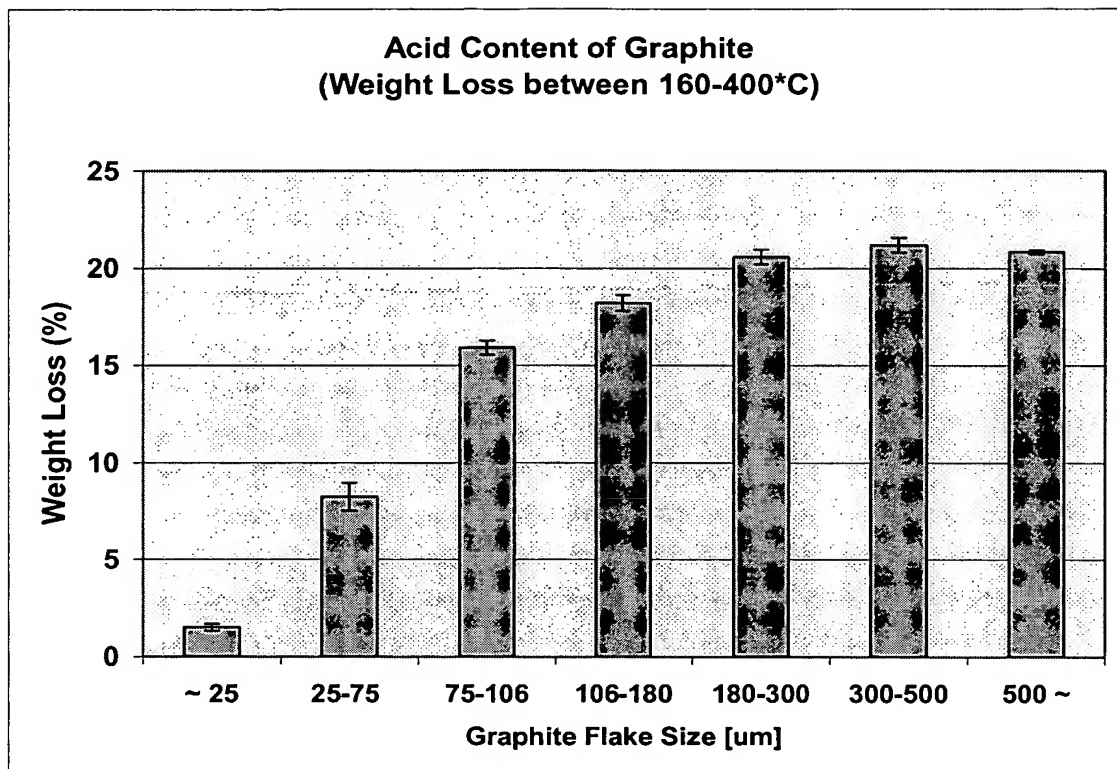
Figure 2.5. The Effect of Size on the Amount of Acid Intercalate Content

2.3.2. Expansion of Graphite Flakes by Microwave

The physical principle of dielectric heating, which includes microwave and radio frequency heating, is based on the transformation of electromagnetic field energy into thermal energy in polar materials. Dipoles of polar materials change their direction by following the direction of the electromagnetic field, causing friction between molecules and transform the applied microwave energy into thermal energy. Microwave process has many advantages over conventional heating such as less energy consumption, faster process, homogeneous and simultaneous heating throughout the whole sample, and higher process capacity. Because of these advantages, the microwave process also offers a considerable cost reduction.

Graphite material is highly conductive and has many pi electrons, which can move throughout the sample when a voltage is applied. Also these electrons can move in the direction of the electromagnetic field when it is applied. This causes vigorous vibration of electrons, leading to the rapid heating of graphite materials. The temperature could reach few hundred degrees Celsius within a few seconds. Thus, the microwave process can provide an alternative method to expand graphite-intercalated compounds.

Figure 2.6 shows the effect of size of graphite flakes on the expansion by microwave processing. 0.1 g of sieved graphite samples were put in sample vials and microwaved at 900 W for 5 seconds. The frequency of the microwave was 2.45 GHz. It showed that the larger the size, the better the expansion. By comparing the heating process, **Figure 2.4**, and the microwave process, **Figure 2.6**, it was shown that microwave process could give the same or better degree of expansion for graphite flakes.
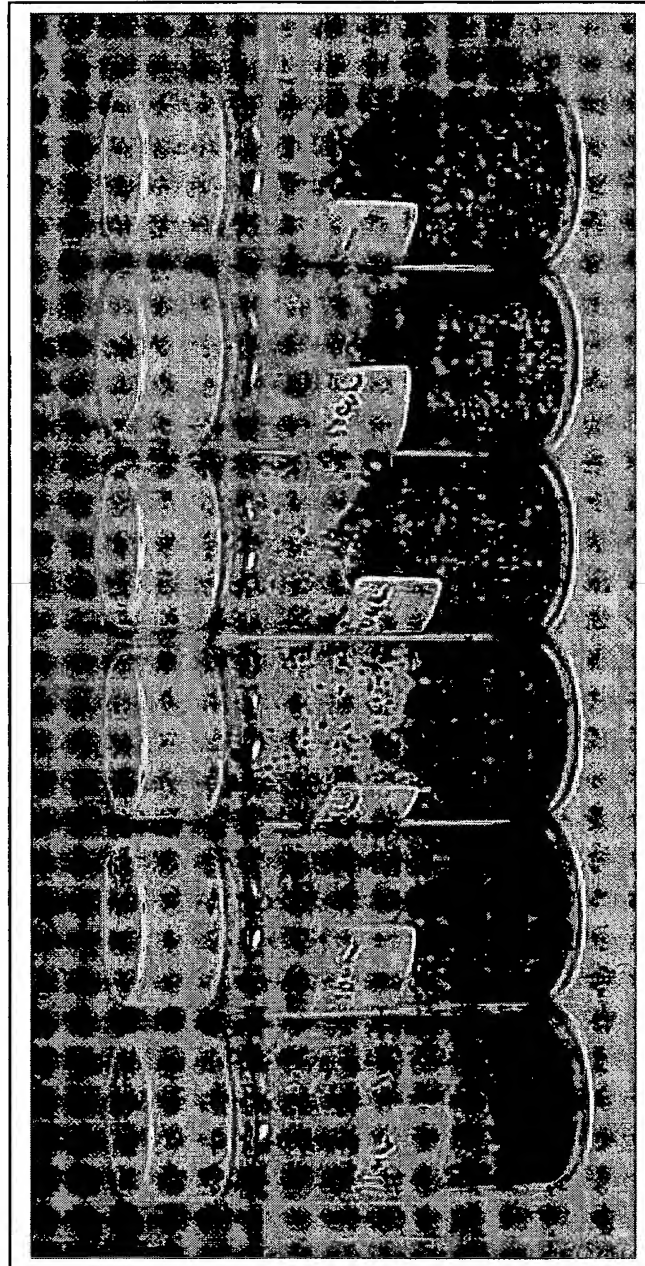
25-75um   75-106um   106-180um   180-300um   300-500um   +500um

Figure 2.6. The Effect of Size on Degree of Expansion (Microwave Process at 1300W)

2.3.3. Comparisons of Conventional Heating and Microwave Process

2.3.3.1. Degree of Expansion

Since graphite flakes have layered structures, they show distinctive peaks in XRD patterns. These XRD data can be used to examine the degree of expansion of GICs. The peak of d002 plane of the as-received 160-50A samples appears as a large sharp peak (**Figure 2.7**) while those of expanded graphite samples became a lot smaller, suggesting that most of the layered structures were destroyed because of the expansion. (**Figure2.8, Figure 2.9**) However, acid intercalated graphite has multiple stage structures from 1 to 5, which means the acid components intercalate in every 1, 2, 3, 4, or 5 layers of graphite. It is impossible to exfoliate all the graphite material into single layers. The peak height of the expanded graphite depends on the process condition. **Figure 2.10** shows the peak height of d002 planes of expanded graphite samples treated under various conditions. It revealed that overall microwave treatment showed a better degree of expansion than conventional heating process, including heating at the temperature of 600°C to 800°C, which is commonly used in the commercial expansion processes.

Also BET surface areas of heat or microwave treated samples were measured to estimate the degree of expansion. **Figure 2.11** shows the results. The surface areas of microwave exfoliated graphite samples were more than 4 times larger than those of the heat exfoliated samples. This result also supports that the microwave process can give a better degree of expansion. Using surface area determined by BET measurements and the average diameter from ESEM images, the thickness and aspect ratio of each sample was calculated. The assumptions used in this calculation were 1) each flake has an octagonal shape, 2) the thickness is constant, and 3) the density of graphite is 2.0 g/cm^3. The results
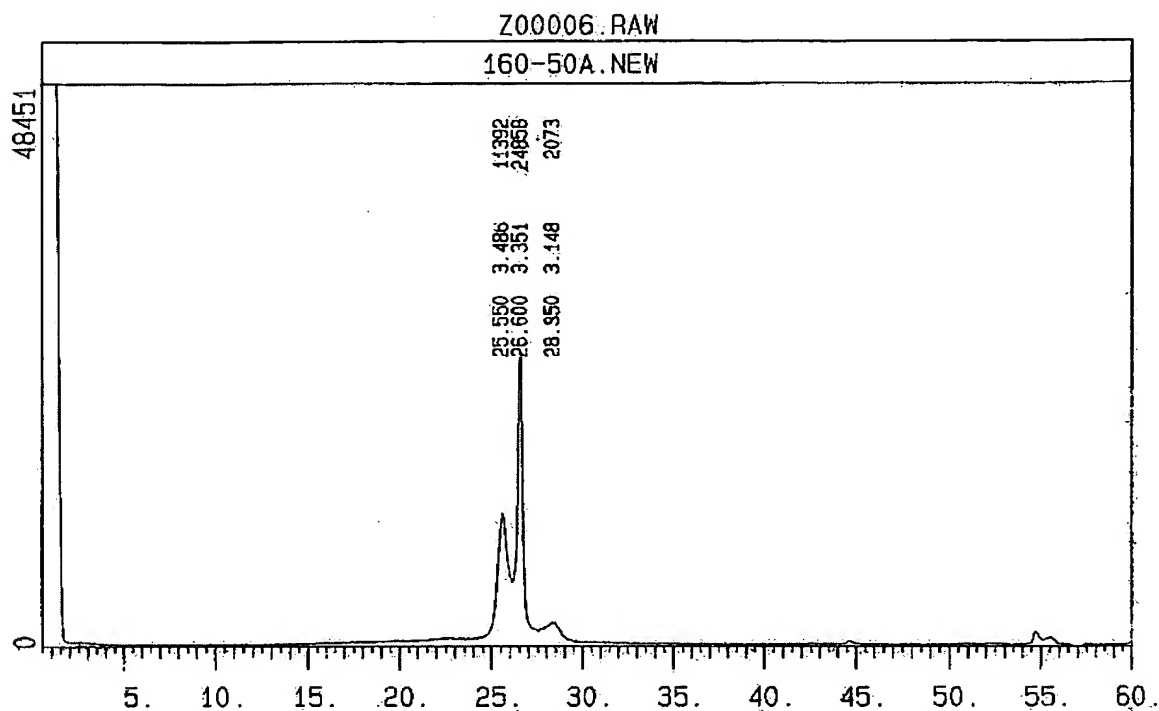
Z00006.RAW

160-50A.NEW

48451

11392
24858
2073

3.486
3.351
3.148

25.550
26.600
28.950

5. 10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60.

Figure 2.7. XRD curves of Graphite Samples. As-received Graphite Sample (160-50A, d002=24858 cps)

Z00040.RAW

900C.3MIN

1074

163

3.370

26.450

5. 10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60.
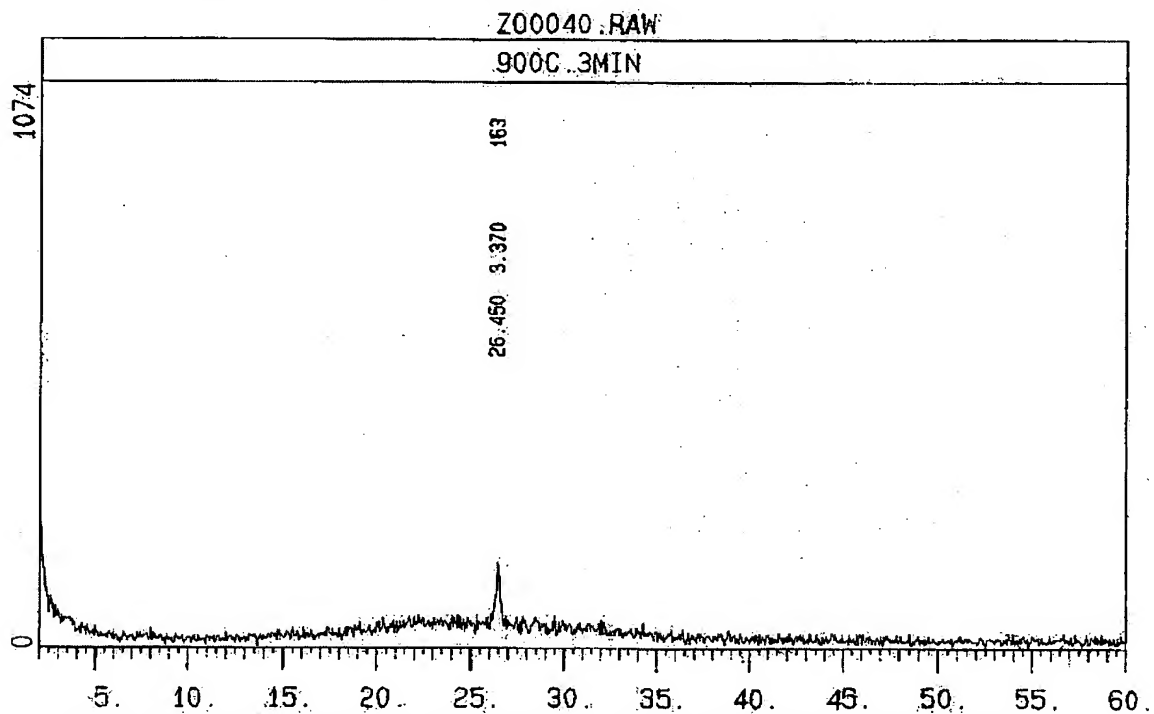
Figure 2.8. XRD curves of Graphite Samples after Expansion by Heating, (900°C for 3min, d002=163 cps)

85
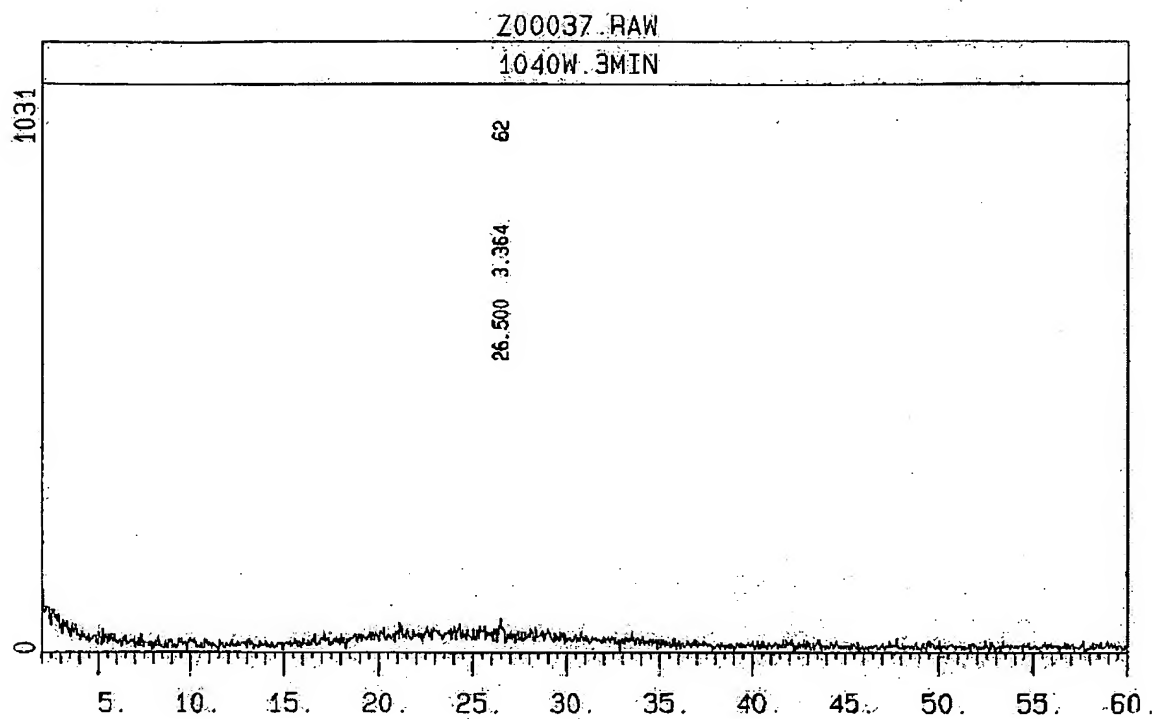
Figure 2.9. XRD curves of Graphite Samples after Expansion by Microwave (1040W for 3min, d002=62 cps)

(A) XRD of Expanded Graphite by Heating
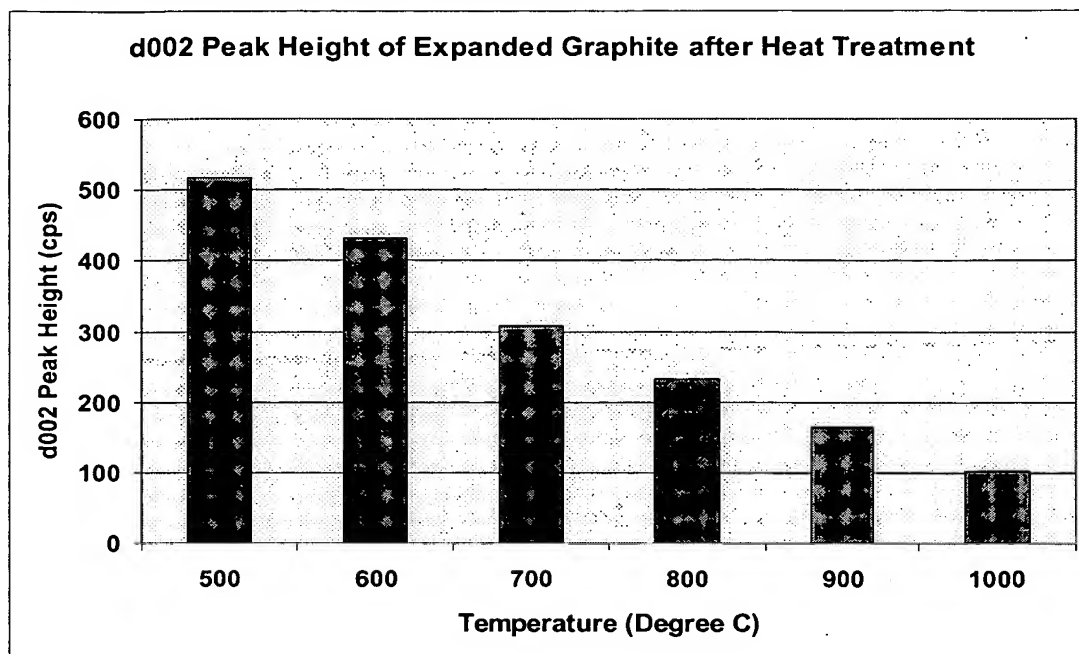
(B) XRD of Expanded Graphite by Heating
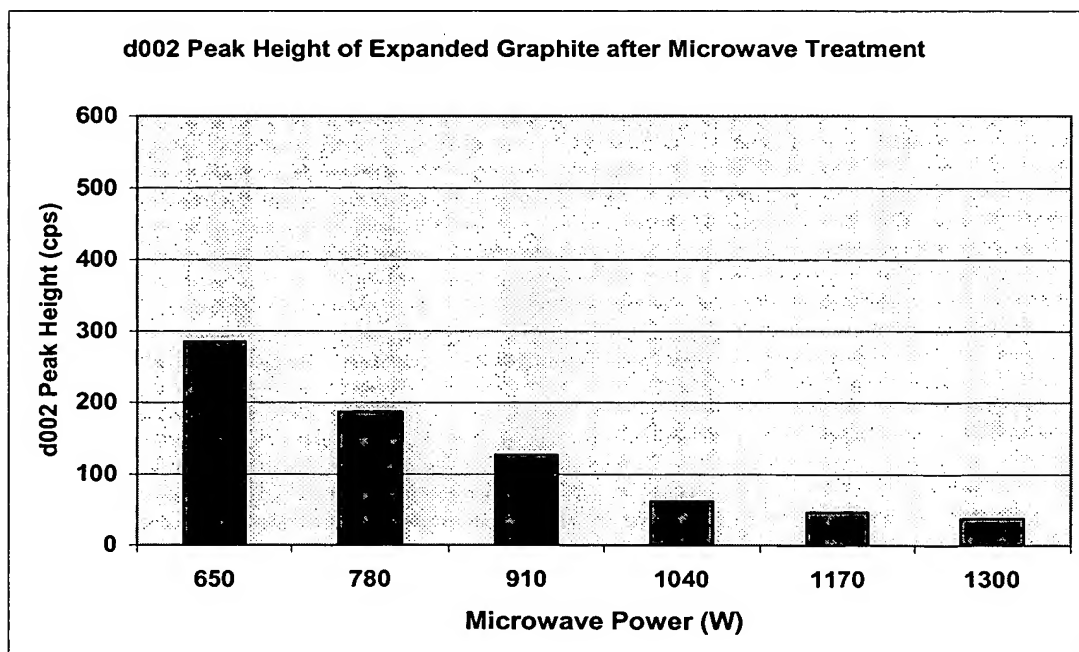
Figure 2.10. d002 Peak Height for Expanded Graphite Treated by Heating (A) or Microwave (B) under various conditions.
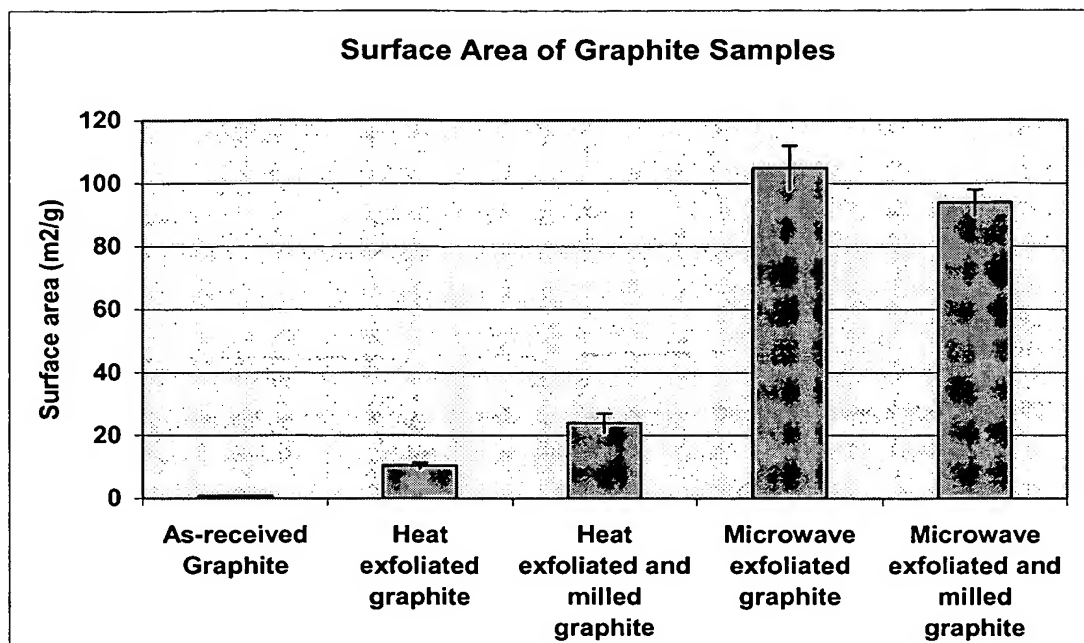
Figure 2.11. Surface Area of Graphite Samples determined by BET measurement

Table 2.1. Thickness and Aspect Ratio of Graphite Samples Calculated from BET Surface Area Data

Sample	Surface Area (m^2/g)	Diameter (um)	Thickness (nm)	Aspect Ratio
As-received 160-50A	0.2	300	5172.4	58.0
Heat Exfoliated Graphite	10.5	15	96.5	155.5
Heat Milled Graphite	24	1.1	45.1	24.4
MW Exfoliated Graphite	105	15	9.5	1573.0
MW Milled Graphite	94	0.86	10.9	78.8

are shown in **Table 2.1**. The thickness of the as-received graphite was estimated around 5 um. The thickness of the Heat Milled Graphite (heat-exfoliated and milled graphite) was estimated around 50 to 100 nm while that of the MW Milled Graphite (microwave-exfoliated and milled graphite) was determined about 9 to 11nm. These results are well matched to the thickness observed in ESEM and TEM images. **(Figure 2.12, 2.13, 2.14)** Judging from these results, it is concluded that microwave process can offer a much better degree of expansion than conventional heating process does at a lower energy consumption and cost.

2.3.3.2. Cleanness of Surface

Although the expansion occurs within a second, there could be some acid components left on graphite surfaces even after treatments, which could cause problems when the expanded graphite materials are used in further applications. To investigate the surface condition of expanded graphite, XPS (X-Ray Photoelectron Microscopy) data were collected and analyzed. **Figure 2.15** shows the sulfur/carbon and nitrogen/carbon ratio of the expanded graphite. Sulfur content suggests the existence of sulfuric acid while nitrogen implies nitric acid. At 600°C treatment, the sulfur and nitrogen components were detected even after 10 minutes of treatment. At 800°C, these components were almost removed from the sample after 5 minutes of treatment. At 1000°C, it required about 2 minutes to remove these components. **Figure 2.16** shows the XPS results of expanded graphite by microwave treatment. In this case, the sulfur and nitrogen component were removed after 2 minutes treatment at 910W and 1300W. This implies that the microwave treatment also has advantage over conventional heating process in terms of removal of the residual intercalates.
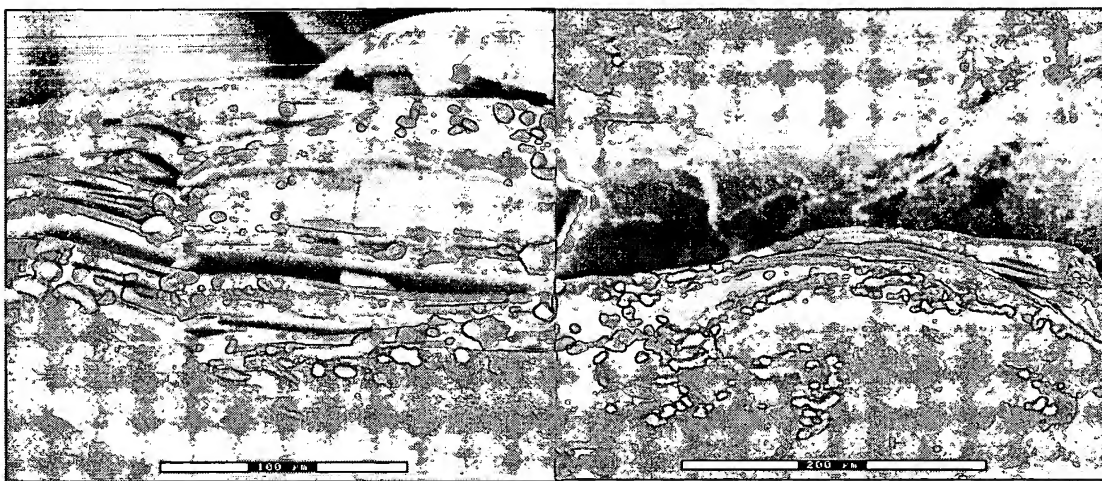
89

Figure 2.12. ESEM Images of As-received Graphite Sample
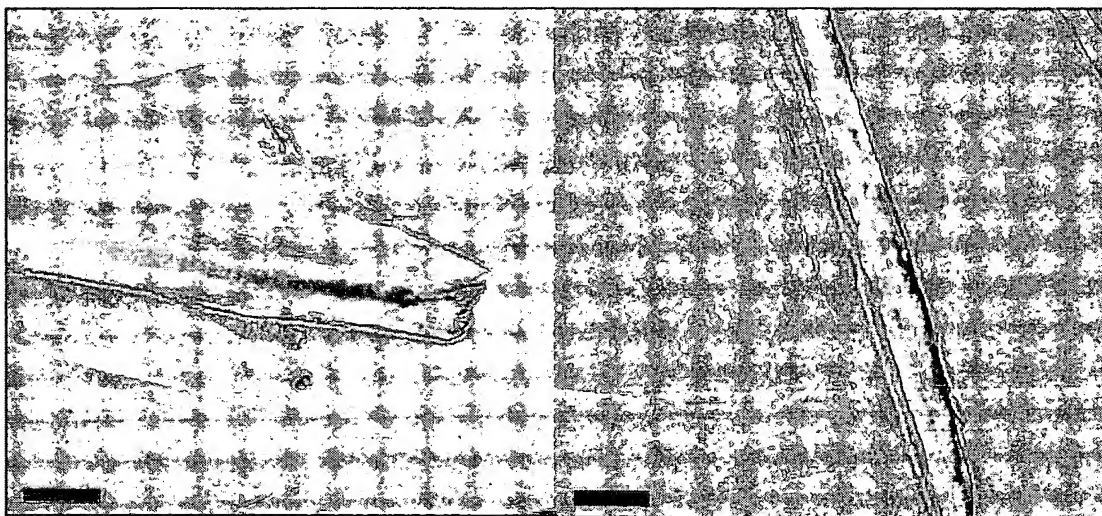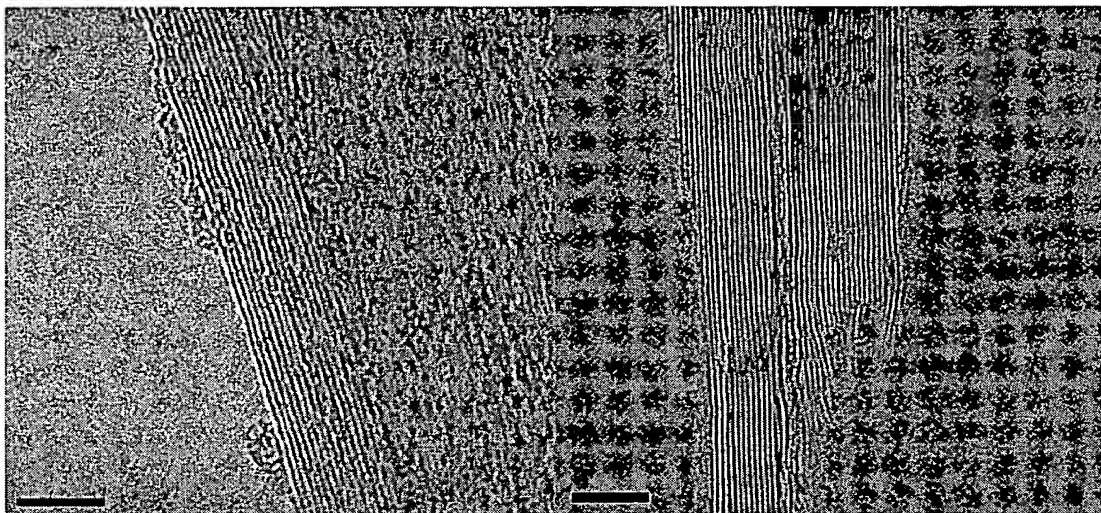**Scale Bar = 100 um (Left), 200 um (Right)**

Figure 2.13. TEM Image of Heat-exfoliated Graphite Sample
Scale Bar = 100 nm (Left, Right)

Figure 2.14. TEM Images of Microwave-exfoliated Graphite Sample
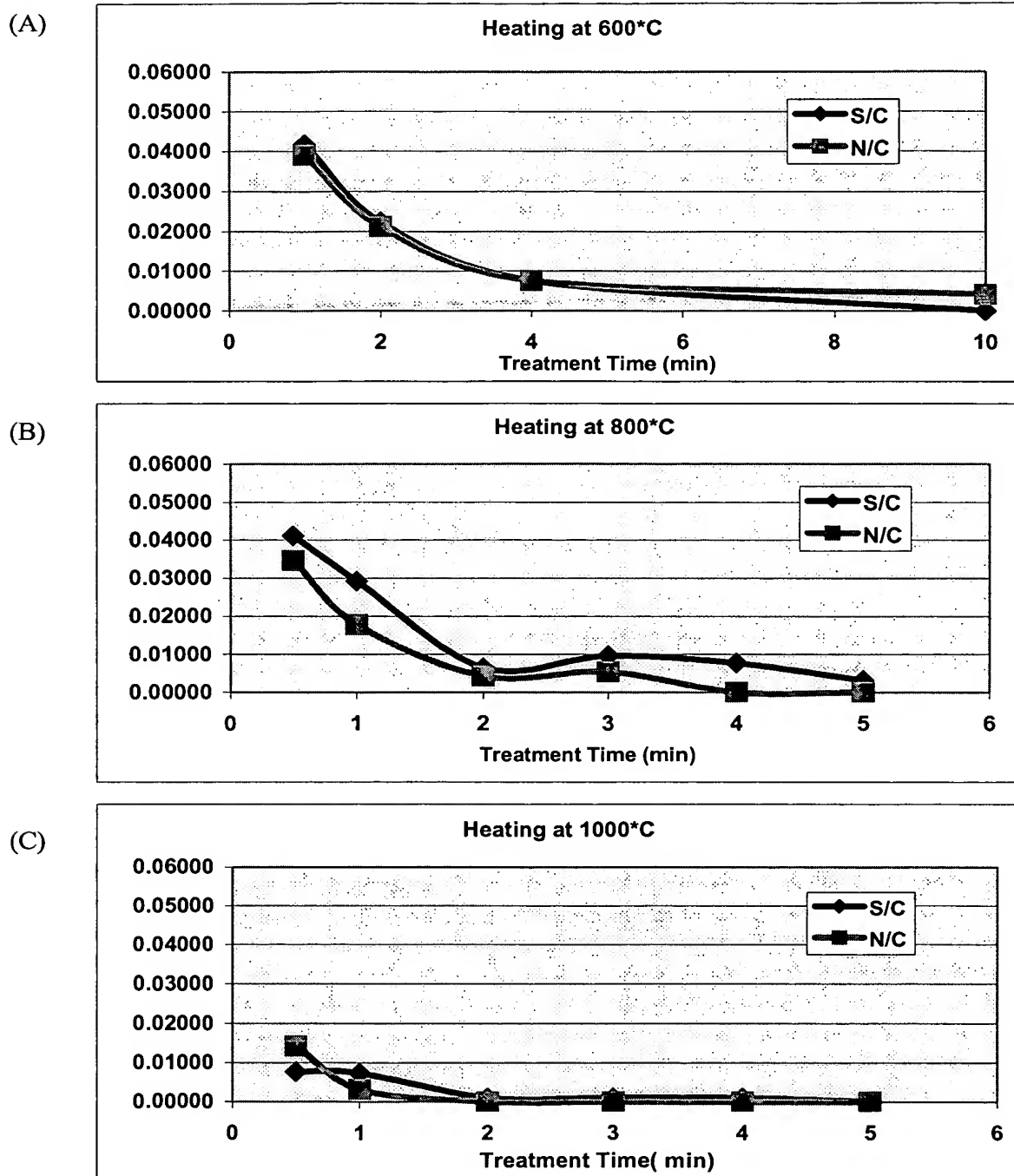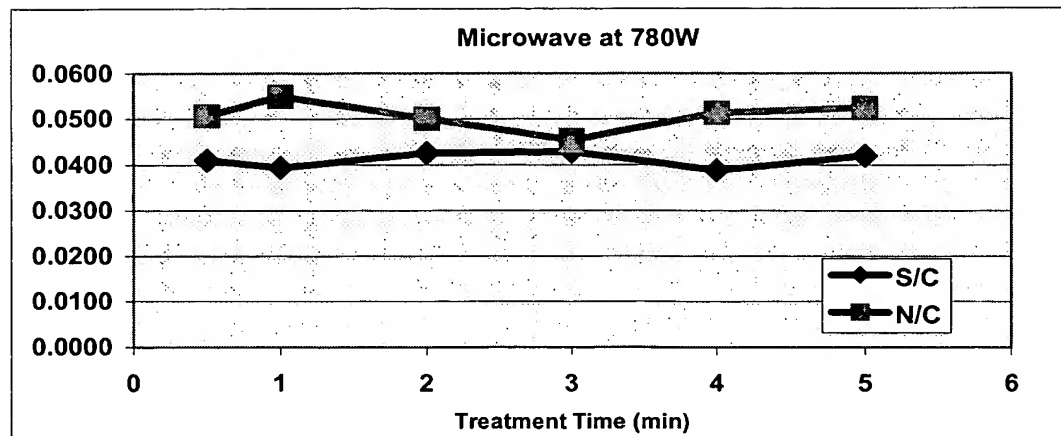**Scale Bar = 5 nm (Left, Right)**

(A)

Heating at 600*C

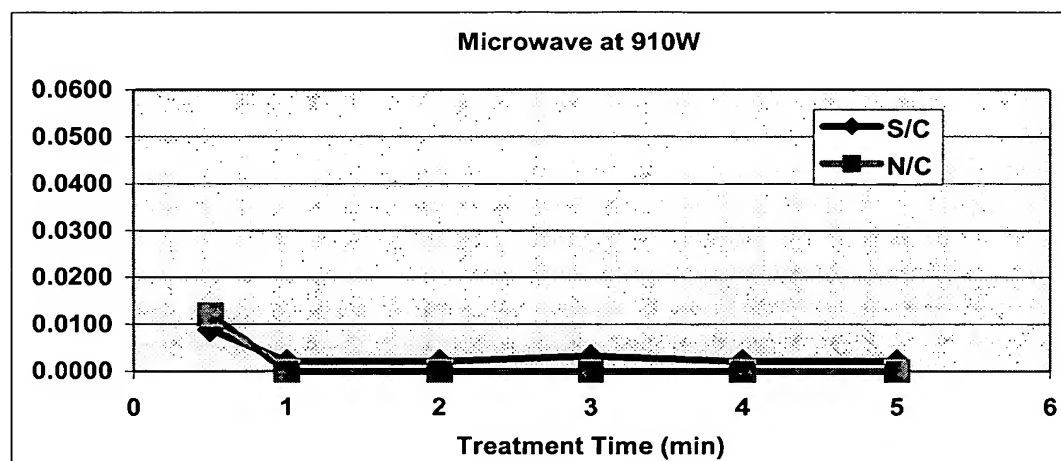(B)

Heating at 800*C

(C)

Heating at 1000*C

Figure 2.15. Acid Components on The Surface of Expanded Graphite under Various Conditions. Heating Process at 600°C (A), 800°C (B), and 1000 °C (C).
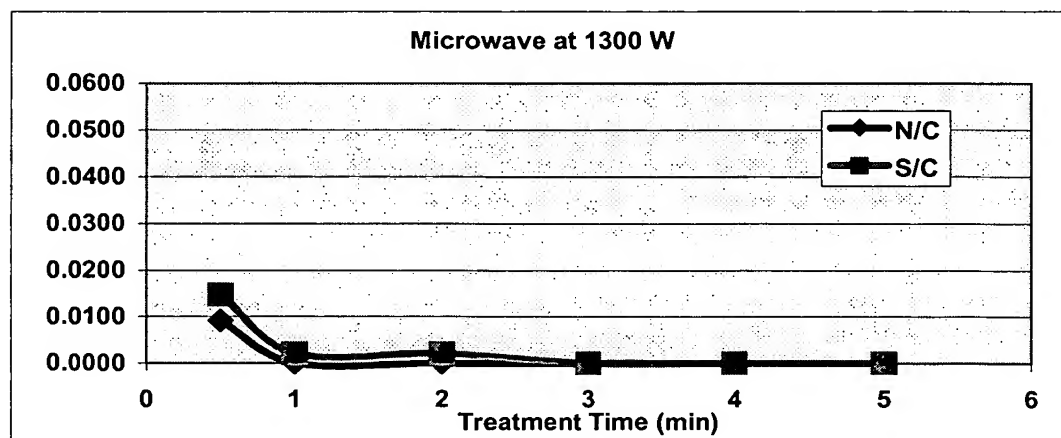
92

(A)

(B)

(C)

Figure 2.16. Acid Components on the Surface of Expanded Graphite under Various
Conditions. Microwave Process at 780W (A), 910W (B), and 1300W(C).

93

2.3.4. Grinding Process for Expanded Graphite

The worm-like graphite samples can be pulverized into small flakes by ultrasonic waves, mechanical grinding, or other methods. **Figure 2.17** shows an ESEM image and **Figure 2.18** shows the size distribution of the graphite particles after pulverization by sonication. 20 g of the expanded graphite sample was dispersed in 2 liters of acetone and pulverized by the 20 kHz ultrasonic wave at 100W for 2 hours. The average size of this sample was 14.25 um.

These samples can be ground into smaller flakes by ball milling, planetary milling, or vibratory milling. **Figure 2.19** shows the ESEM images of graphite flakes after 72 hours of vibratory ball milling. The slurry was made around 12 to 15 wt% of graphite in 2-propanol. **Figure 2.20** shows the size distribution of the sample. The average size became 0.86 um.

2.4. Conclusions

The microwave and heat exfoliation processes of GICs were investigated and compared. It revealed that the microwave process could give a better degree of expansion and a cleaner surface at a lower cost. These expanded graphite samples were pulverized and milled into sub-micron size graphite flakes. SEM, TEM and AFM images showed that the average size of graphite became 0.86um and the thickness became10 nm. The cost of this new nano-size graphite material was estimated around $5/lb. [CHAPTER 6] Because of its superior mechanical, electrical, thermal properties and cost effectiveness, this material is expected to be used in a variety of applications such as nanocomposites, secondary batteries, and fuel cells.
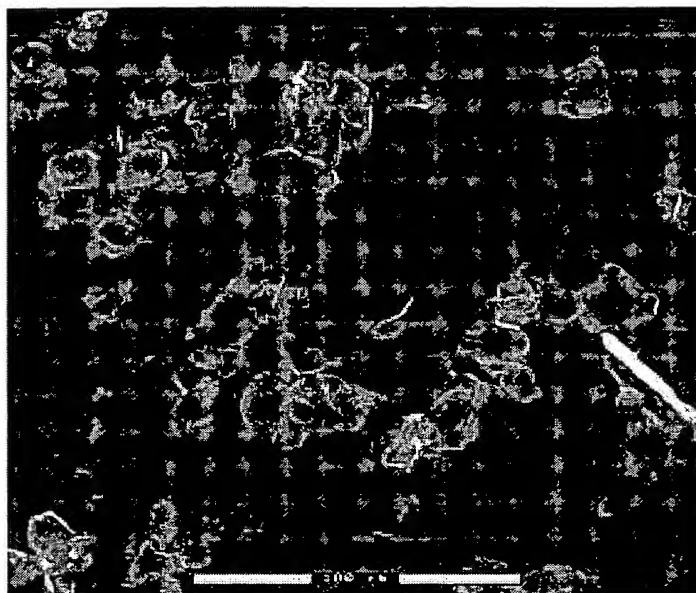
Figure 2.17. ESEM image of Graphite Fakes after Exfoliation and Pulverization (Scale Bar = 100um)
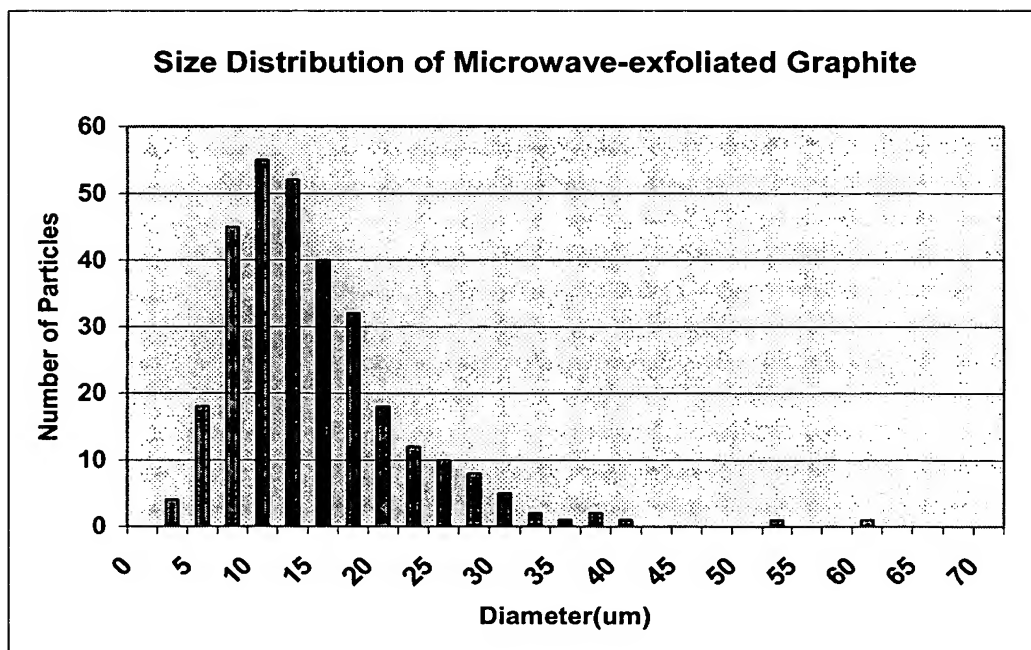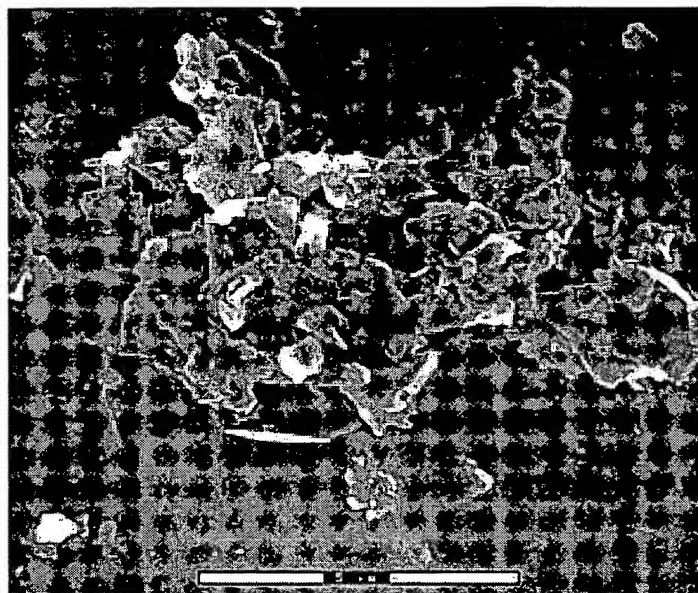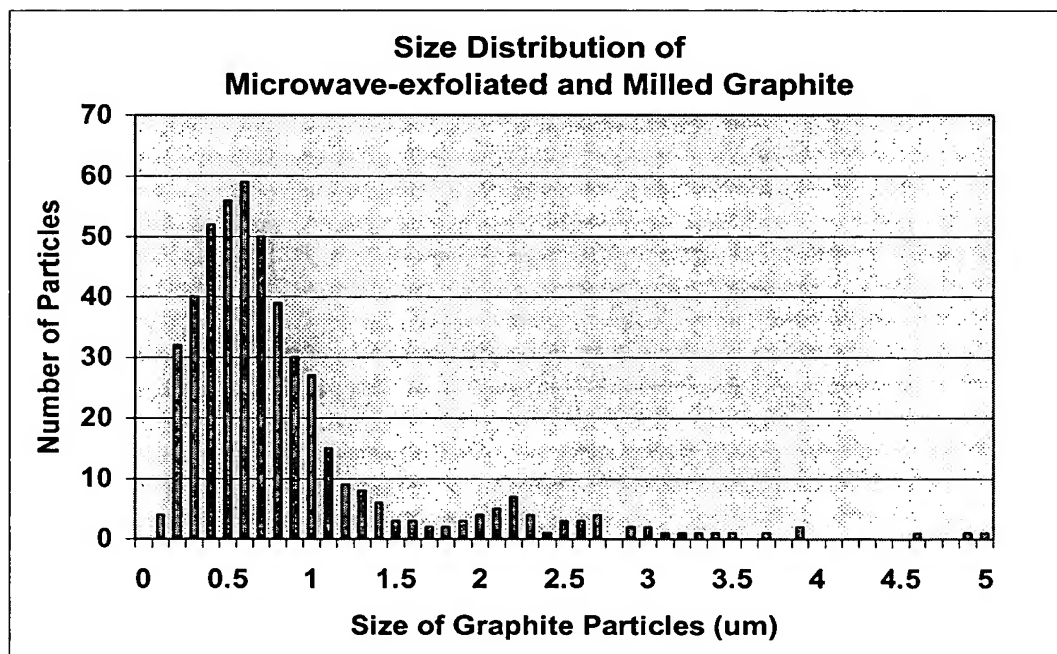

Figure 2.18. Size Distribution of Graphite Particle after Exfoliation and Pulverization by Sonication, Average Size = 14.25 um (Standard Deviation = 7.53 um)

Figure 2.19. ESEM image of Graphite Fakes after Ball Milling (Scale Bar = 5um)

Figure 2.20. Size Distribution of Graphite Particle after Ball Milling (72 hr) Average Size = 0.86 um (Standard Deviation = 0.73 um)

2.5. Reference

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